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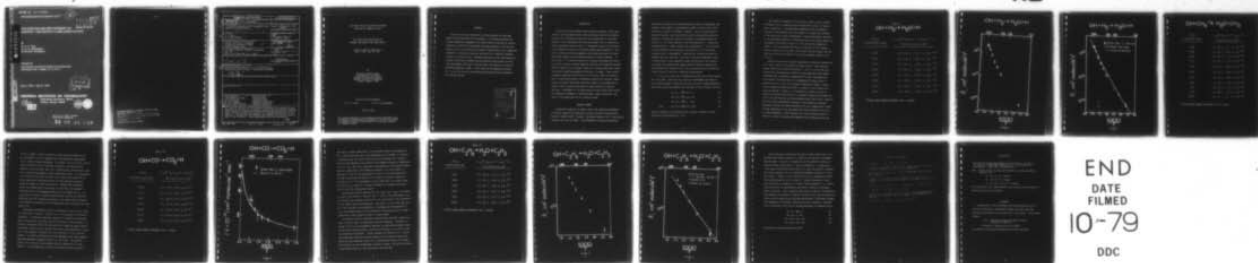
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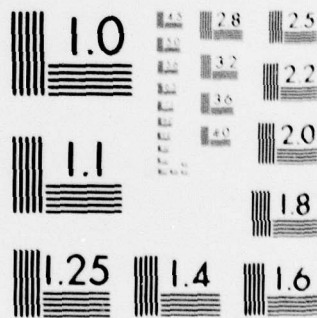
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INTERIM SCIENTIFIC REPORT NO. 2



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THE KINETICS AND SPECTROSCOPY OF AIRCRAFT AND ROCKET PLUME CONSTITUENTS

By

Dr. F. P. Tully

Dr. A. R. Ravishankara

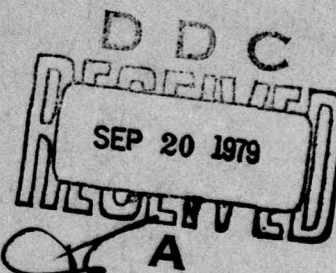
Co-Principal Investigators

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GEORGIA INSTITUTE OF TECHNOLOGY

Engineering Experiment Station

Atlanta, Georgia 30332



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Utilizing the technique of flash photolysis-resonance fluorescence the rate constants for the reactions of hydroxyl radicals (OH) with hydrogen, methane, carbon monoxide and ethane were measured at elevated temperatures as high as 1020K. Distinct curvature was observed in the Arrhenius plots for all four reactions. The measured rate constants were compared with previous measurements in the literature. Future measurement plans were outlined.												

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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THE KINETICS AND SPECTROSCOPY OF
AIRCRAFT AND ROCKET PLUME CONSTITUENTS

Interim Scientific Report No. 2
June 1, 1978 - May 31, 1979

By:

Molecular Sciences Group
Electromagnetics Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Co-Principal Investigators:

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Dr. A. R. Ravishankara

July 31, 1979

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ABSTRACT

During the past year particularly striking progress has been made toward the dual objectives of this program: 1) to measure absolute rate constant temperature dependences for radical-molecule reactions of specific importance to modelling of combustion and plume processes in aircraft and rockets; and 2) to contribute to the general understanding of the temperature dependence of bimolecular reactions, particularly as related to observed curvature in Arrhenius plots. Improved sensitivity in the flash photolysis-resonance fluorescence technique was achieved and high-accuracy rate constant measurements were made in the heretofore only marginally accessible 500-1000K temperature regime. Kinetic data for the important reactions $\text{OH} + \text{H}_2$, CH_4 , CO , and C_2H_6 was obtained and promising future experiments were thereby defined.

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INTRODUCTION

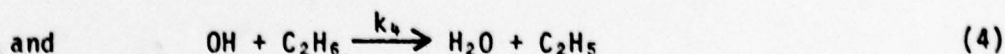
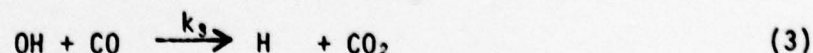
Aircraft and rocket exhaust plumes provide an energetic, highly non-uniform, local environment within which microscopic physical and chemical processes act to dictate the nature of bulk observations of the medium. Analyses of fuel performance and tracking procedures rely on modelling of those contributing processes which, in combination, govern the efficiency of the propulsion system or surveillance method under examination. Chemically, reactions within the combustor and afterburning within the plume place heavy demands on the estimating prowess of kinetic modellers. In most cases, it is simply not possible to calculate which among the myriad of possible processes are most important (and thus which among the possible molecular species are of greatest concern)—an extensive data base, promoting realistic modelling parameter limitations, is needed. From a kinetic standpoint, optimized acquisition of this data base implies the measurement of oxidant/fuel/reaction intermediate reaction rate constants needed directly for model input and/or required as bases for the generation of 'global' kinetic equations applicable to entire families of chemical reactions. Improvement of the understanding of those factors which govern the temperature dependence of combustor/plume relevant bimolecular reactions is the primary goal of this research program.

PROGRESS SUMMARY

Historically speaking, our modern view of the temperature dependence of the rate constant for bimolecular gas-phase reactions originated with Arrhenius' model in 1889.¹ Arrhenius' postulated equation, $k(T) = A \exp(-E_a/RT)$, endured as law into the 1960s. The development of improved experimental

techniques applicable over extended temperature ranges of measurement then spawned a large number of intercomparable studies and led to the initial clear case of failure of Arrhenius' equation. Even up through the past few years, however, such failures were typically characterized merely by noting, for a particular reaction, substantial disagreement between the $\log k(T)$ vs. $1/T$ slopes obtained as the high-temperature ($T > 1000K$) and low-temperature ($T < 500K$) straight-line extrapolations. It has not been, in the past decade, that curvature in the $\log k(T)$ vs. $1/T$ (so-called Arrhenius) plot is unacceptable; theoretically, curvature has been considered likely for some time. The lack of sufficient congruence of data in either (high or low) temperature regime and the nearly total absence of reliable rate constant data between 500K and 1000K has delayed until quite recently and limited to just a very few reactions even the empirical smooth joining of high and low temperature measurements.

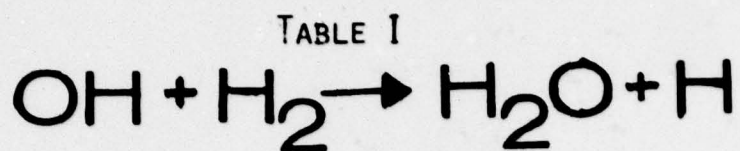
It is precisely that void in elementary reaction rate constant measurements from 500K - 1000K that has inspired the development and growth of this research program. During the past year, accurate extended temperature range rate constant measurements have been made for the following reactions:



Distinct curvature in the Arrhenius plot, varying in degree, has been observed for each Reaction (1) - (4).

Our results for Reaction (1) are listed in Table I and are plotted individually and in combination with selected other results in Figures 1 and 2, respectively. Our measurements demonstrate that the degree of curvature in the Arrhenius plot for Reaction (1) exceeds that predicted by the expression of Cohen and Westberg.² Cohen and Westberg's empirical fit was generated primarily by interpolative joining of immense numbers of measurements (not shown in Figure 2) in the low and high temperature regimes. Thus, even though the kinetics of Reaction (1) has received enormous attention over the years, the previous scarcity of data from 500-1000K has limited the reliability of the best obtainable empirical fits for $k_1(T)$.

Absolute reaction rate constant measurements obtained for Reaction (2) are listed in Table II and plotted in Figures 3 and 4. Many important general features are evident from Figure 4. First, it can be seen that straight-line extrapolations of either the low-temperature based (NASA, troposphere and stratosphere) recommendation³ or the high-temperature based (Peeters and Mahnen best fit) recommendation⁴ produce order of magnitude errors in $k_2(T)$ in the opposing temperature regimes. Clearly, even for approximate modelling efforts, curvature in the Arrhenius plot cannot be ignored. Second, it is interesting to contrast the data of Zellner and Steinert⁵ with Zellner's subsequently obtained forced empirical fit⁶ to the existing high- and low-temperature data (solid line in Figure 4). Using the direct experimental technique of flash photolysis-resonance absorption, Zellner and Steinert measured $k_2(T)$ up to temperatures of 892K. At lower temperatures, this data agrees well with the empirical fit, but, at higher temperatures, their measured $k_2(T)$ values exceed the best fit values by a factor increasing with temperature and already more than two



(°K) TEMPERATURE	(CM ³ MOLEC ⁻¹ SEC ⁻¹) K _{BIMOLECULAR} *
298	(6.08 ± .37) × 10 ⁻¹⁵
499	(1.15 ± .08) × 10 ⁻¹³
576	(2.34 ± .18) × 10 ⁻¹³
648	(3.84 ± .18) × 10 ⁻¹³
739	(7.64 ± .56) × 10 ⁻¹³
838	(1.30 ± .10) × 10 ⁻¹²
904	(1.86 ± .35) × 10 ⁻¹²
992	(1.99 ± .19) × 10 ⁻¹²

* STATED ERROR BOUNDS REPRESENT THE 2σ VALUES.

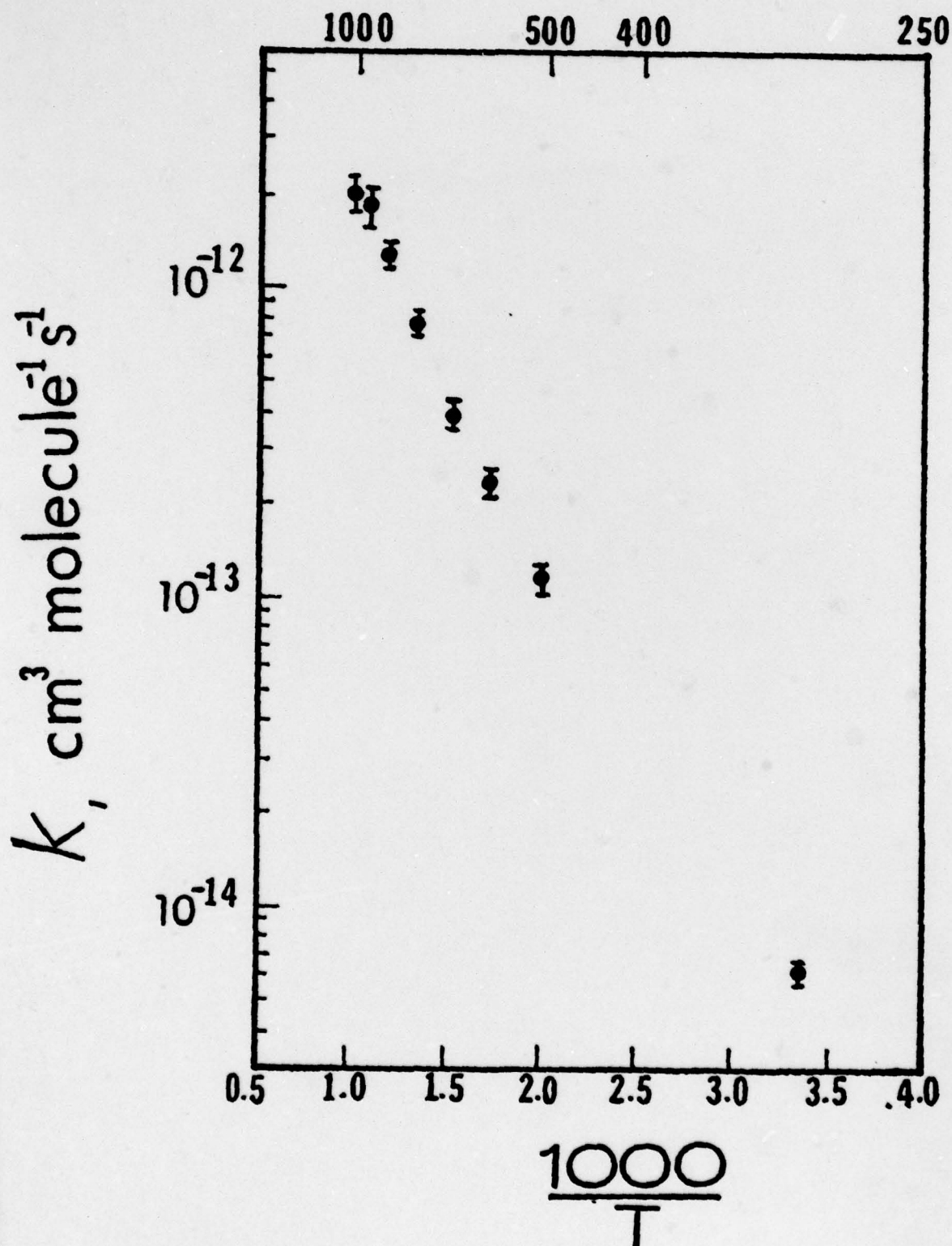


FIGURE 1
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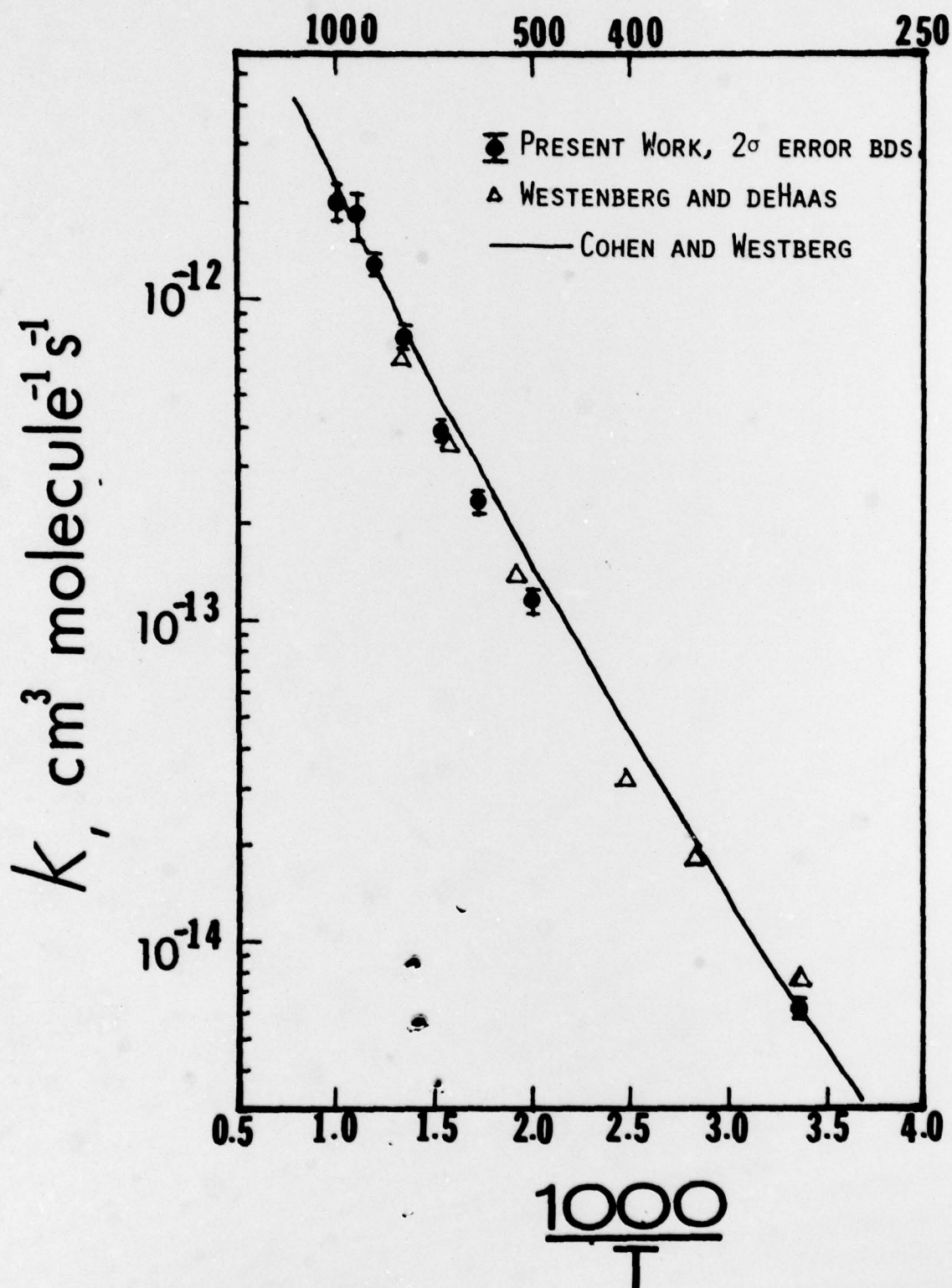
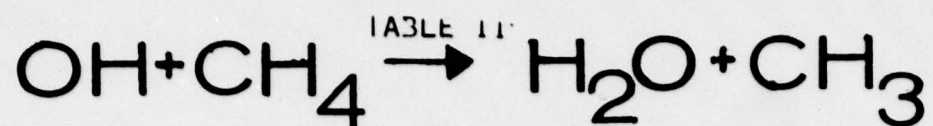
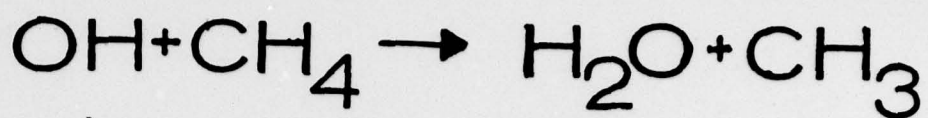


FIGURE 2
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(°K) TEMPERATURE	(CM ³ MOLEC ⁻¹ SEC ⁻¹) K _{BIMOLECULAR} *
298	(7.50 ± .6) x 10 ⁻¹⁵
398	(4.73 ± .45) x 10 ⁻¹⁴
448	(8.07 ± 1.1) x 10 ⁻¹⁴
511	(1.45 ± .12) x 10 ⁻¹³
529	(1.67 ± .06) x 10 ⁻¹³
600	(3.14 ± .40) x 10 ⁻¹³
619	(2.75 ± .44) x 10 ⁻¹³
696	(5.78 ± .58) x 10 ⁻¹³
772	(8.37 ± 1.5) x 10 ⁻¹³
915	(1.50 ± .15) x 10 ⁻¹²
1020	(2.0 ± .2) x 10 ⁻¹²

* STATED ERROR BOUNDS REPRESENT THE 2σ VALUES.



$k, \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

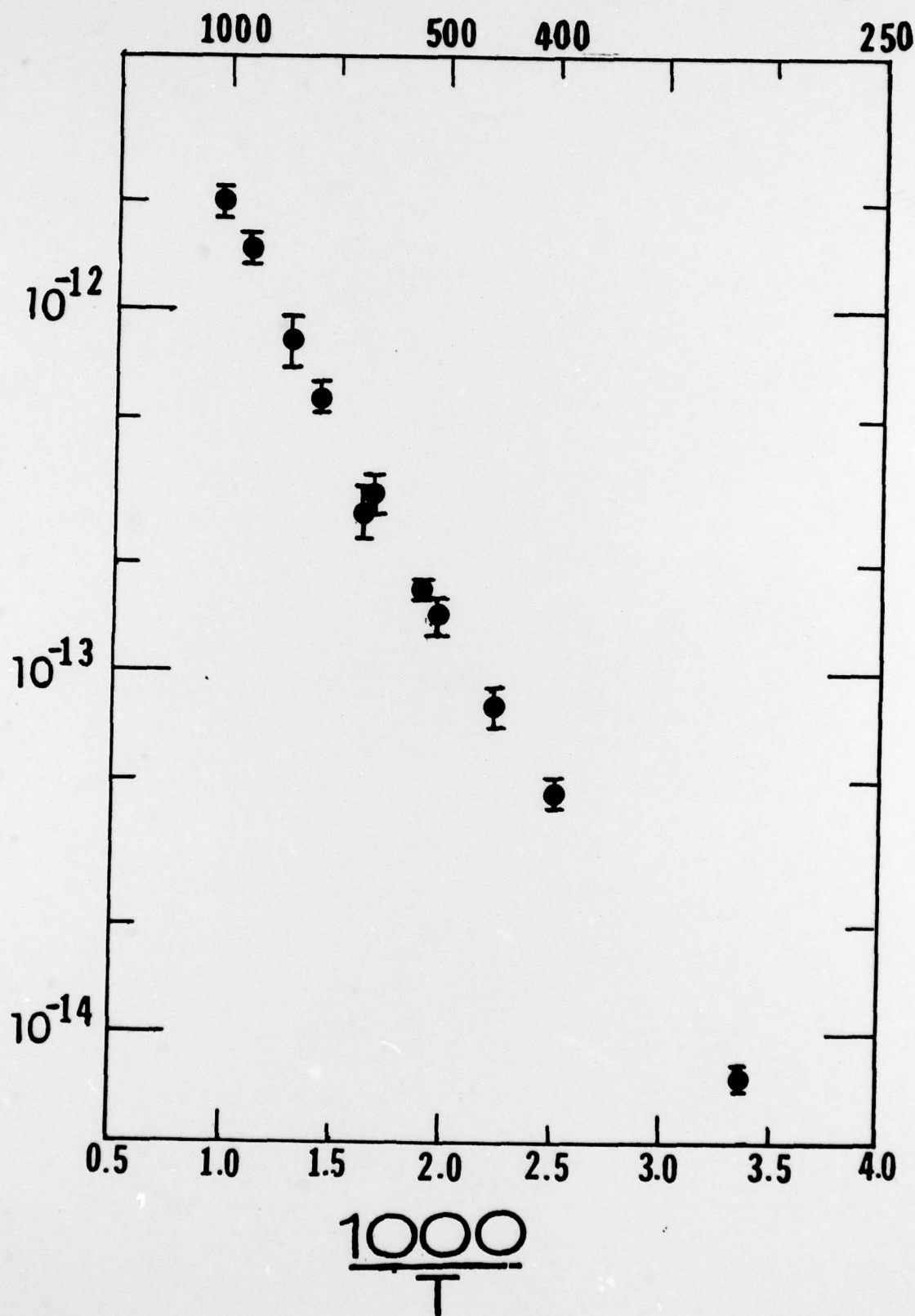


FIGURE 3

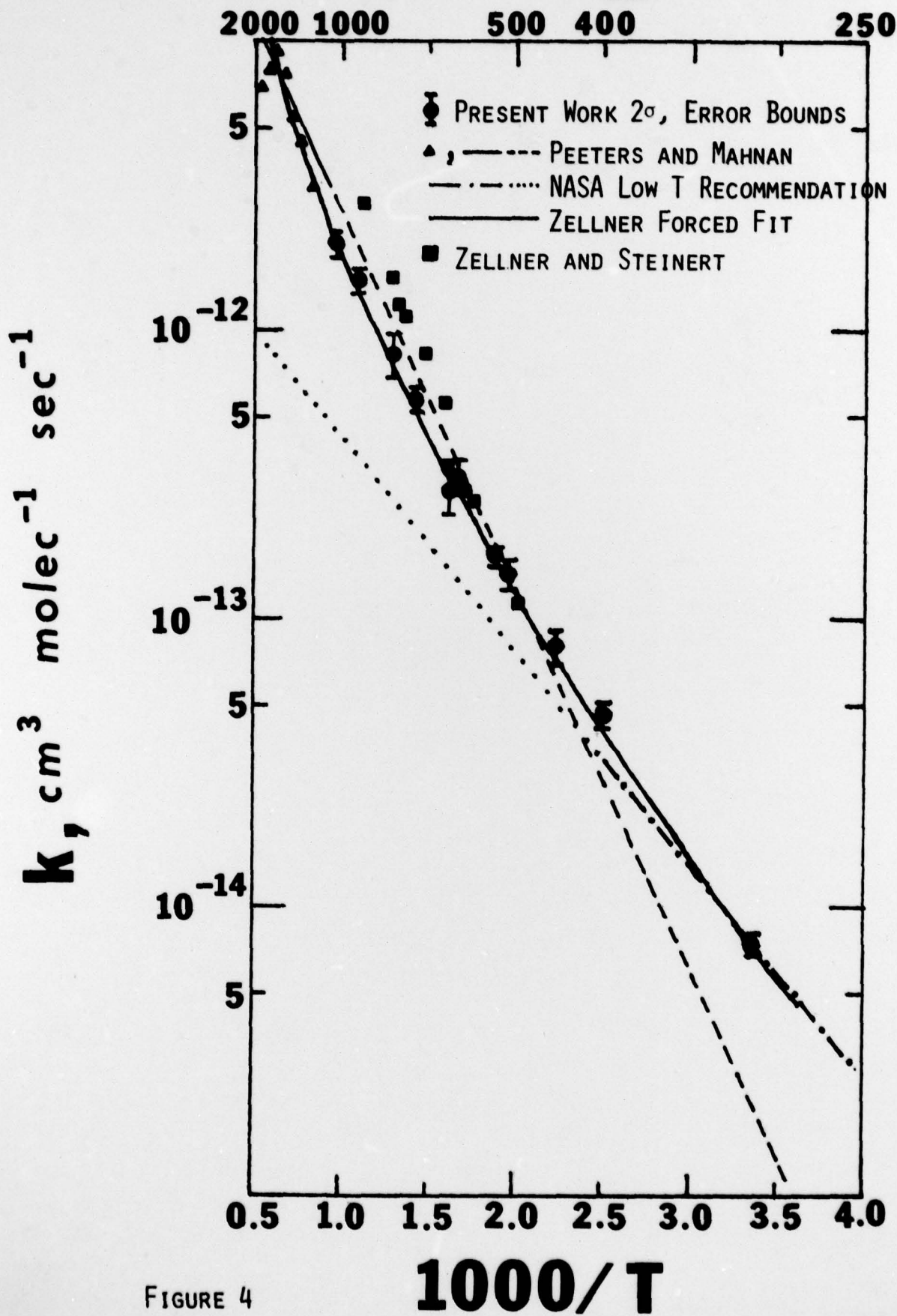
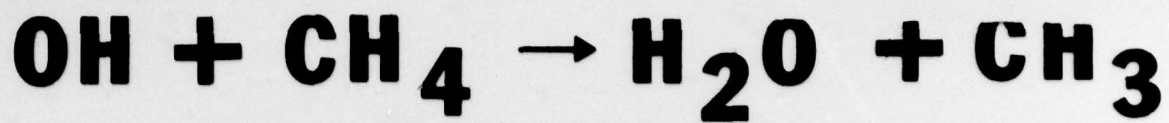
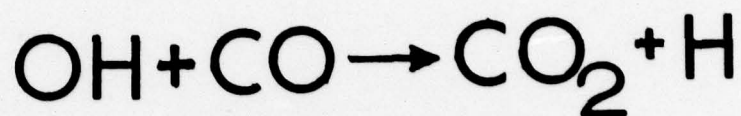


FIGURE 4

at 900 K; indeed, Zellner was forced to attach minimal weighting to his own measurements to attain agreement with high-temperature measurements such as those of Peeters and Mahnen. In contrast, our $k_2(T)$ values reported above lie dead-on Zellner's empirical expression, verifying both the adequacy of the functional form, $k(T) = AT^n \exp(-E_a/RT)$, and the basic soundness of previous measurements in both temperature regimes. Our flash photolysis-resonance fluorescence technique, then, appears more appropriate to higher temperature investigations than the flash photolysis-resonance absorption method of Zellner and Steinert. Although both experiments measure the disappearance of OH radicals in real time, the absorption technique monitors the difference between two large numbers $[(I_{t=0} - I_t)/I_{t=0}]$, and thus requires larger OH concentrations to match the statistics obtainable from the fluorescence technique. Such larger radical concentrations enhance the probability of OH disappearance due to processes other than Reaction (2).

Experimental measurements of $k_3(T)$ for Reaction (3) are listed in Table III and plotted in Figure 5. The $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ reaction is of extreme importance. In combustion processes, Reaction (3) represents the principal mode of conversion of CO to CO_2 ; since this reaction is very exothermic, its kinetics considerably impact the time profile for combustive energy release, and thereby, factors such as ignition, acceleration and propagation of flames. Also in the atmosphere, Reaction (3) is the principal $\text{CO} \rightarrow \text{CO}_2$ conversion pathway; its kinetics and possible pressure dependence thus impact numerous important atmospheric chemicals cycles (e.g., $\text{NO} \rightarrow \text{NO}_2$). The pictorial effect of the curvature in the Arrhenius plot for Reaction (3) is quite dramatic. At low temperatures, the activation energy for this reaction is

TABLE III



(°K)	(CM ³ MOLEC ⁻¹ SEC ⁻¹)
TEMPERATURE	K _B BIMOLECULAR*
298	(1.45 ± .10) × 10 ⁻¹³
511	(1.77 ± .08) × 10 ⁻¹³
607	(1.89 ± .15) × 10 ⁻¹³
703	(2.03 ± .26) × 10 ⁻¹³
800	(2.39 ± .12) × 10 ⁻¹³
922	(3.04 ± .40) × 10 ⁻¹³
992	(3.11 ± .40) × 10 ⁻¹³

* STATED ERROR BOUNDS REPRESENT THE 2σ VALUES.

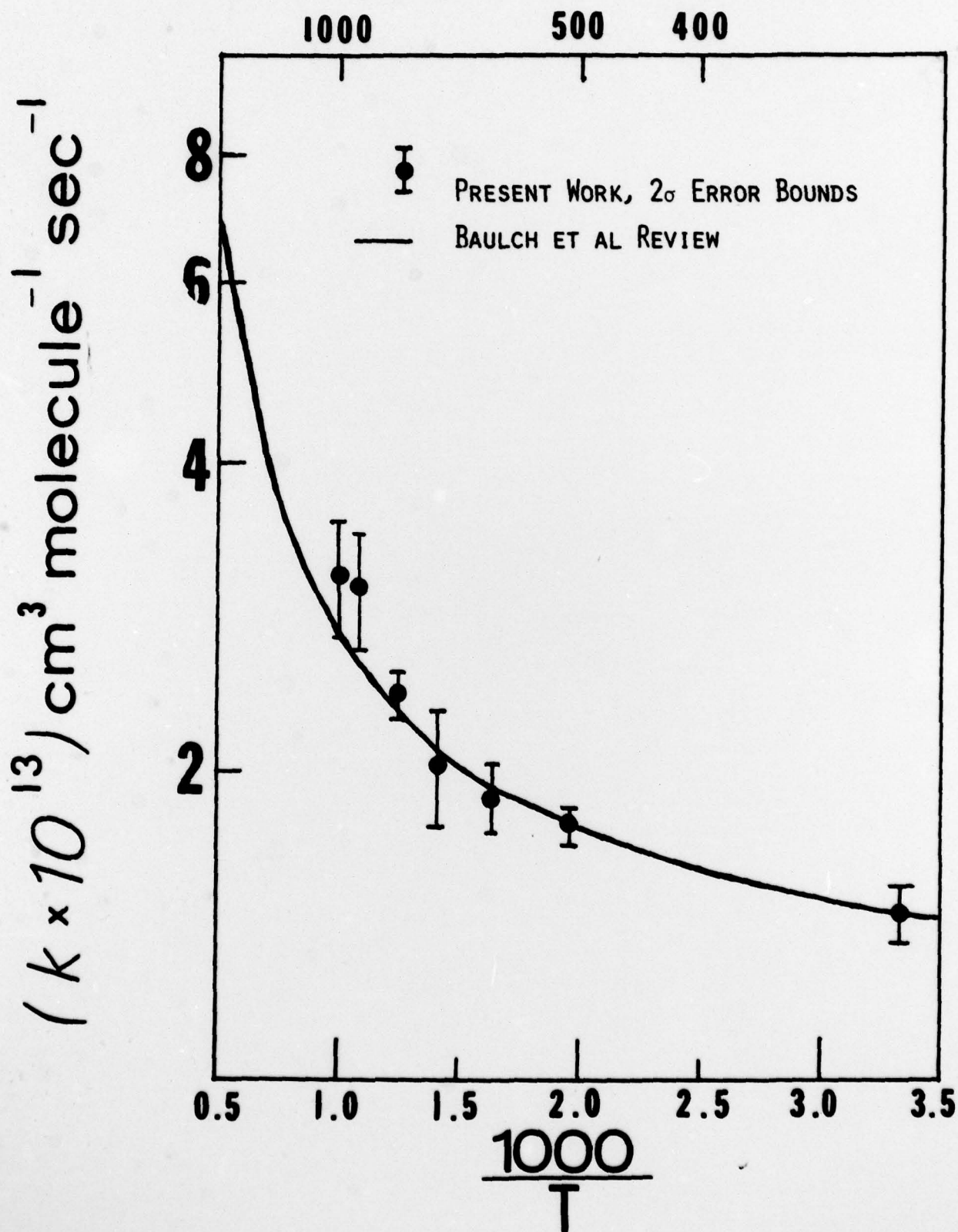
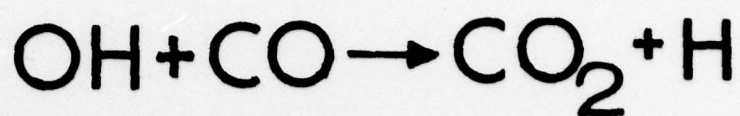


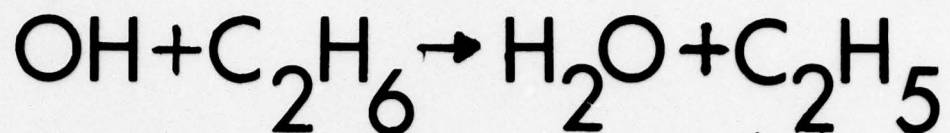
FIGURE 5

near zero; at higher temperatures, $k_3(T)$ increases rapidly with temperature. [It is worth noting here that visual comparisons of the 'degree' of curvature in Arrhenius plots for several reactions can be misleading; for a reaction where the low-temperature rate constant itself depends strongly on temperature, e.g., $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$, substantial high-temperature rate constant enhancement may be perceived as only moderate curvature.] As in our studies of Reactions (1) and (2), our measurements of $k_3(T)$ fill the gap between 500 K and 1000 K and verify the adequacy of the empirical forced fit expression of Baulch, et al.⁷ Our measurements of $k_3(T)$ above 900 K lie slightly above the solid line in Figure 5; it would be worthwhile to remeasure and extend $k_3(T)$ to the 1200 K temperature regime.

Rate constant data for Reaction (4), $\text{OH} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5$, is tabulated in Table IV and plotted in Figures 6 and 7. Prior to these measurements, the only reliable rate constants existing for this reaction were a few measurements at and slightly above room temperature. Once again, it can be seen from Figure 7 that straight-line extrapolation of low-temperature measurements⁸ results in an underestimation of the bimolecular rate constant $k_4(T)$ at higher temperatures; concave upward curvature is again evident.

The chemical kinetics experiments described above represent valuable new input to current models of hydrocarbon combustion processes. Reactions (1) through (3) are of such fundamental importance to hydrocarbon oxidation chains that accurate characterization of these $k_i(T)$ functions is, in itself, a goal of considerable significance. Kinetic estimates for Reactions (1) - (3) pervade hydrocarbon combustion modeling efforts; use of incorrect input could modify the bulk observable results of a simulated model process to an extent which implies that the assumed model structure is wrong - this may be the case, or the problem could be in the inaccuracy of the data base.

TABLE IV



$(^{\circ}\text{K})$ TEMPERATURE	$(\text{CM}^3 \text{ MOLEC}^{-1} \text{ SEC}^{-1})$ $k_{\text{BIMOLECULAR}}^*$
297	$(2.59 \pm .21) \times 10^{-13}$
400	$(7.71 \pm .76) \times 10^{-13}$
499	$(1.58 \pm .10) \times 10^{-12}$
609	$(2.61 \pm .33) \times 10^{-12}$
697	$(3.65 \pm .25) \times 10^{-12}$
800	$(5.07 \pm .34) \times 10^{-12}$

* STATED ERROR BOUNDS REPRESENT THE 2σ VALUES.

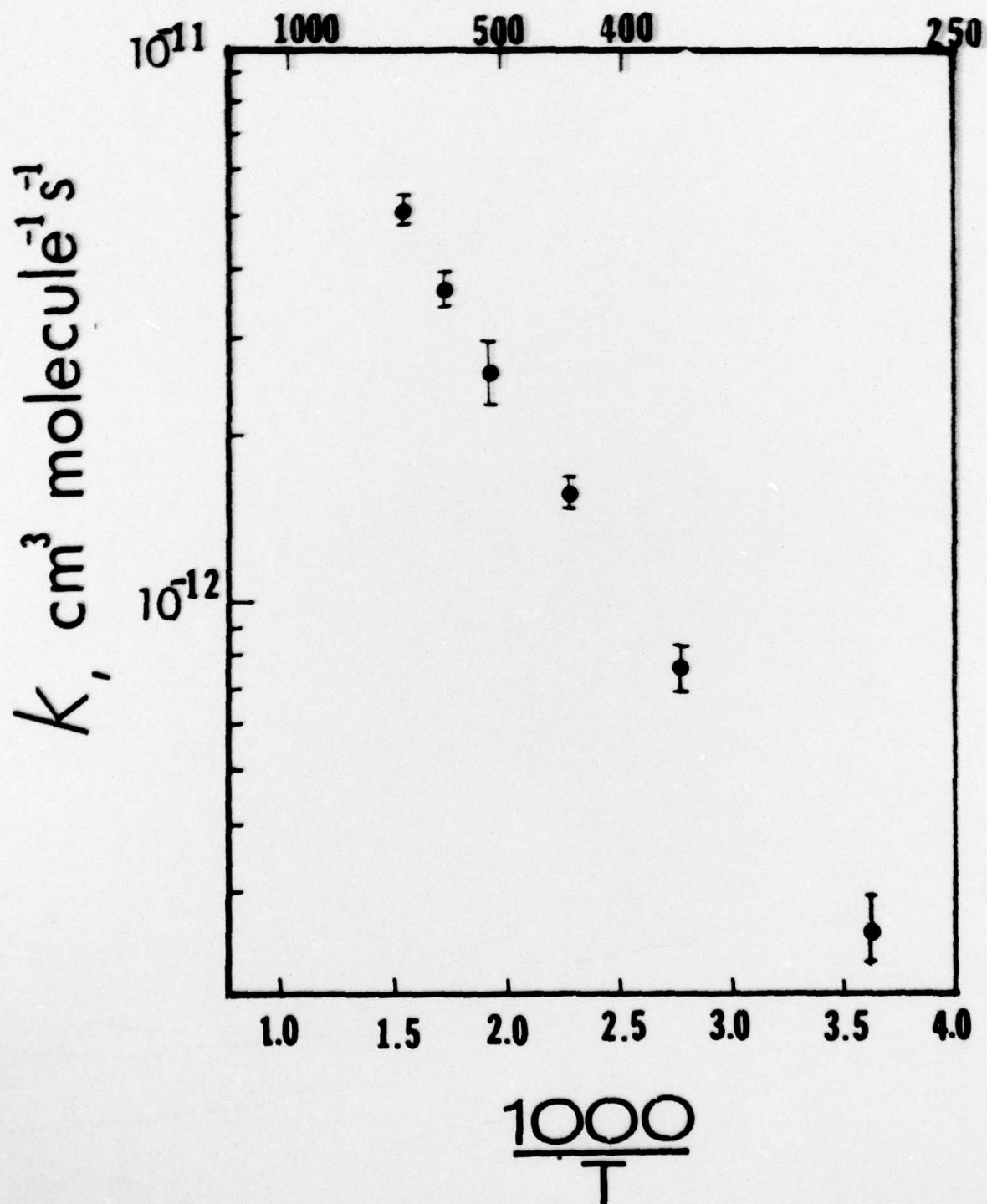
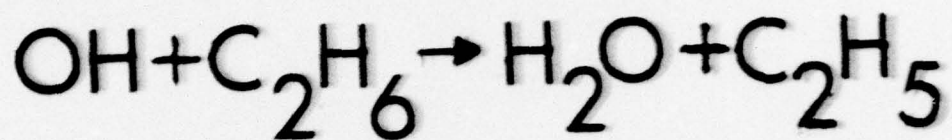


FIGURE 6

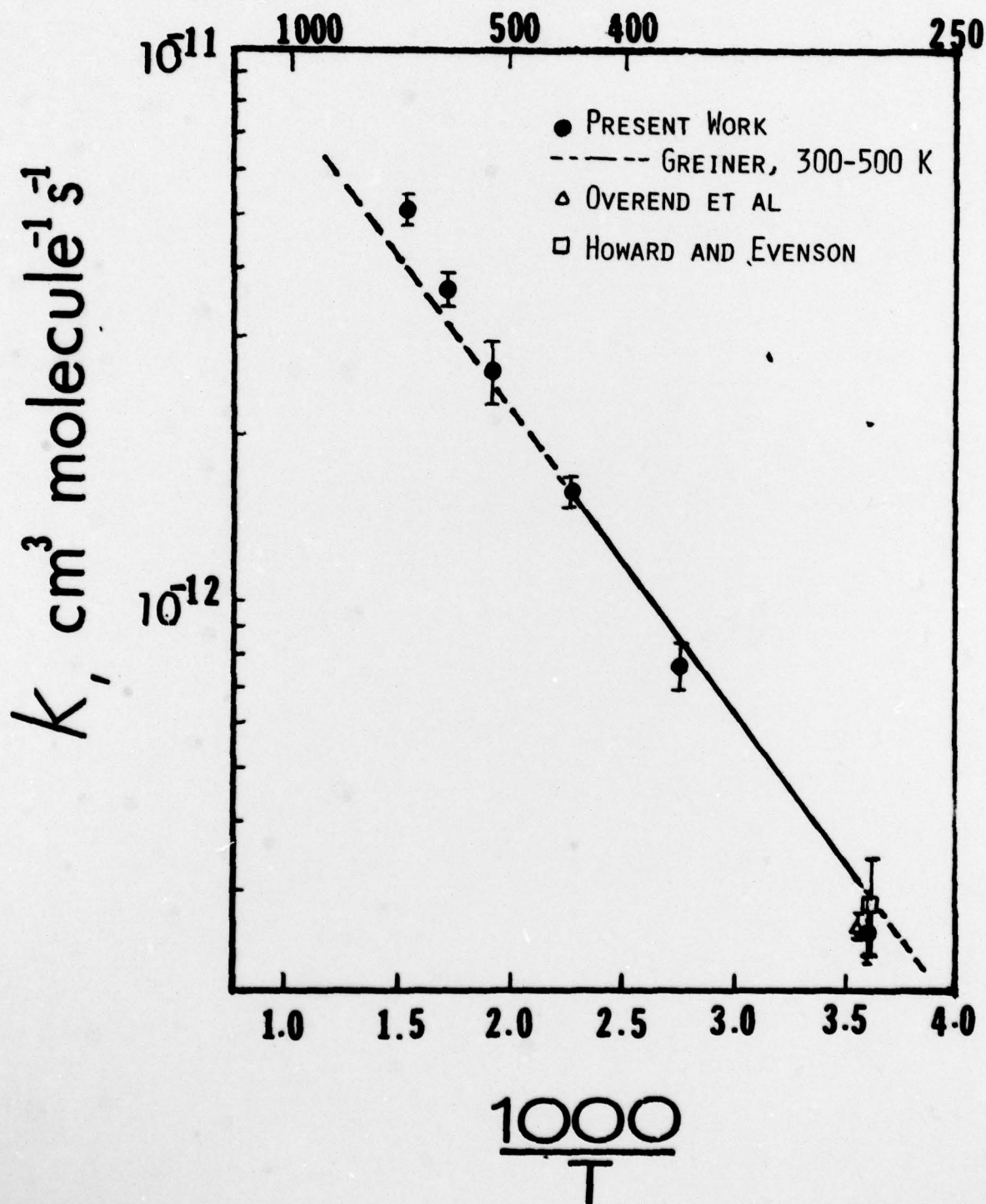
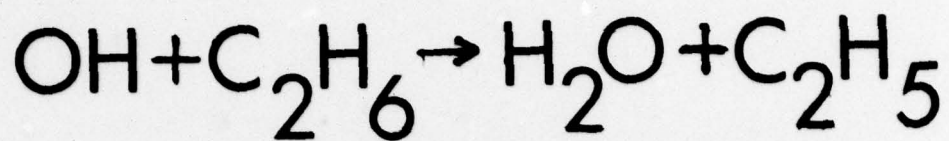
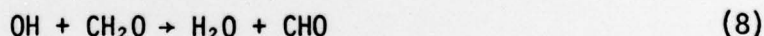
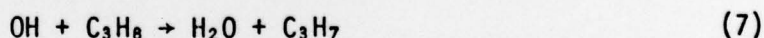
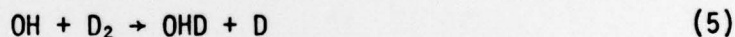


FIGURE 7

Yet one should not assume that the value of these results (and of our developed experimental technique) is limited to the numerical achievements detailed above. Typically, the complexity of the chemistry involved in a combustion and/or plume process is nearly overwhelming. In recent years it has become increasingly obvious that it is simply not possible to measure the kinetic parameters for all contributing elementary reactions in a complex process. Indeed, if such a data base did exist, computational limitations would prevent its full utilization. Increasing attention is thus being focused on the generation of 'global' kinetic equations, i.e., kinetic expressions which are approximately applicable to families of analogous chemical reactions. Such a viewpoint then argues the need for investigations which emphasize the effects of chemical structure on the rates of reactivity; studies aimed at generating an improved understanding of the general temperature dependence of bimolecular reaction rates must be pursued. Investigations of Reactions (1)-(4) and our planned experiments on processes such as



represent such structure-motivated studies.

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PUBLICATIONS

"Absolute Rate Constant Measurements of the Reactions of OH with H₂, CH₄, and CO at Intermediate Temperatures," F. P. Tully and A. R. Ravishankara, J. Chem. Phys. (in preparation).

NOTE: Ideally we hope to group the reporting of our data according to structure, e.g.,

- 1) OH + H₂, D₂ → Products
- 2) OH, OD + CO → Products
- 3) OH + CH₄, C₂H₆, C₃H₈ → Products

The likelihood of this format depends on the rapidity with which data for Reactions (5)-(7) can be obtained.

PERSONNEL

Although most of these experiments have been performed by the Co-Principal Investigators, undergraduate student assistants have made significant contributions to the execution of this program. In particular, students

K. Carr - part-time assistant and Special Projects
Researcher in Chemistry

R. Thompson - Cooperative Division Student

have benefited the program and benefited from their experience.